

AD-A192 809

THE INFRARED SPECTRA OF SURFACE METAL ATOM VIBRATIONS  
SNIFTIRS STUDIES IN. (U) UTAH UNIV SALT LAKE CITY DEPT  
OF CHEMISTRY S PONS ET AL. 30 JUL 86 TR-59

1/1

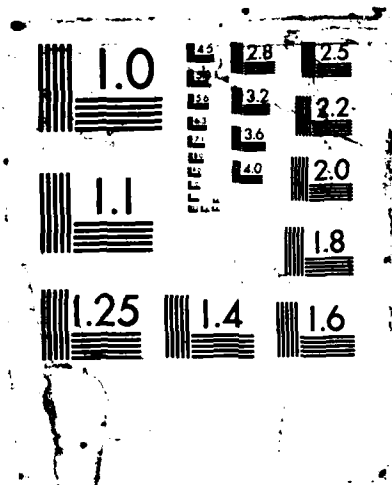
UNCLASSIFIED

N00014-83-K-0470

F/G 20/5

NL





AD-A192 809

4

DTIC FILE COPY

OFFICE OF NAVAL RESEARCH

Contract N00014-83-K-0470-P00003

Task No. NR 359-718

TECHNICAL REPORT # 59

The Infrared Spectra of Surface Metal Atom Vibrations.  
SNIFTIRS Studies in the Far Infrared Region using  
Time Resolved FTIR Techniques

By

Stanley Pons, J. Li, J. Daschbach, J. Smith, M. Morse

Prepared for Publication in  
Journal of Electroanalytical Chemistry

University of Utah  
Department of Chemistry  
Salt Lake City, Utah 84112

July 30, 1986

Reproduction in whole or in part is permitted for  
any purpose of the United States Government.

This document has been approved for public release  
and sale; its distribution is unlimited.

DTIC  
ELECTE  
S APR 14 1988 D  
H

054

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 59	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) The Infrared Spectra of Surface Metal Atom Vibrations. SNIFTIRS Studies in the Far Infrared Region using Time Resolved FTIR Techniques		5. TYPE OF REPORT & PERIOD COVERED Technical Report # 59
7. AUTHOR(s) Stanley Pons, J. Li, J. Daschbach, J. Smith, M. Morse		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Utah Department of Chemistry Salt Lake City, UT 84112		8. CONTRACT OR GRANT NUMBER(s) N00014-83-K-0470-P0003
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Chemistry Program - Chemistry Code 472 Arlington, Virginia 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Task No. NR 359-718
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE July 30, 1986
		13. NUMBER OF PAGES
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) IR spectroelectrochemistry, Time Resolved Spectroscopy, Metal Atom Spectroscopy, infrared radiation ←		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) IR spectra of metal atoms on electrodes is discussed.		

*J. Electroanal. Chem.* 00 (1986) JEC08616  
Elsevier-Quota S.A., Lausanne - Printed in The Netherlands

**AUTHOR****Short communication****THE INFRARED SPECTRA OF SURFACE METAL ATOM VIBRATIONS  
SNIFTIRS STUDIES IN THE FAR INFRARED REGION USING TIME  
RESOLVED FTIR TECHNIQUES**

DASCHBACH

JIANGUO LI, JOHN DASCHBACH, JERRY J. SMITH \*, MICHAEL D. MORSE  
and STANLEY PONS \*\*

*Department of Chemistry, University of Utah, Salt Lake City, UT 84112 (U.S.A.)*

(Received 16th April 1986; in revised form 28th May 1986)

Studies of the vibrations of pure metals have historically been pursued by inelastic neutron scattering (which is sensitive to vibrations of the bulk crystal) and more recently by high-resolution electron energy loss spectroscopy, HREELS (which is more sensitive to vibrations of the metal surface). Direct infrared absorbance techniques provide advantages over both of these methods, since they may be used in more hostile environments (such as at the interface between metal and chemical solutions). They have rarely been applied with much success, however, because of the very effective shielding of the electromagnetic radiation by the metal conduction electrons. This results in an exponential damping of the radiation field as it enters the metal phase, with typical skin depths ( $1/e$  damping distances) of only a few tens of nm. This damping improves the sensitivity of infrared absorption measurements to the surface vibrations as opposed to bulk phonons, but limits the magnitude of the absorbance considerably. In this report we demonstrate that reflection infrared vibrational spectroscopy may be used to observe the vibrational structure of metallic species deposited on a metal surface which is under electrochemical control.

The surface FTIR spectroscopic technique SNIFTIRS [1] has been shown to be useful for the observation of the vibrational structure of monolayer (or less) quantities of materials adsorbed at the surface of metal electrodes while under electrochemical control. We have now extended the method by modifying the cell and detector design to permit observations in the far infrared region, even below  $100\text{ cm}^{-1}$ . In addition, a signal/timer/controller/sequencer and associated software has been developed to allow time resolved infrared spectral measurements to be recorded with  $10\text{ }\mu\text{s}$  resolution [2].

Keywords:

\* Permanent address: Naval Weapons Center, Physics Division, China Lake, CA 93555, U.S.A.

\*\* To whom correspondence should be addressed.

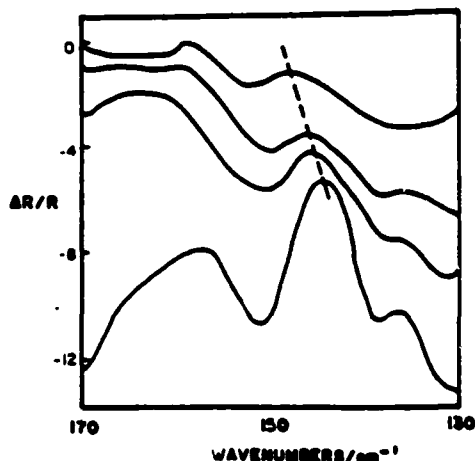


Fig. 1. Surface far infrared difference spectrum of the system described on 130–170  $\text{cm}^{-1}$  region as a function of electrode potential. The curves represent potentials of (top to bottom)  $-1.70$  V,  $-1.90$  V,  $-2.60$  V, and  $-2.90$  V respectively. Reference potential  $-1.50$  V.

Underpotential, solid solution, alloy formation, and bulk metal deposition studies were made for lithium deposited on gold from acetonitrile solution. At potentials between  $-2.40$  and  $-2.60$  V, lithium adatoms are underpotentially deposited on a polycrystalline gold surface where they are oxidized rapidly by trace water to solid lithium hydroxide. Between  $-2.60$  and  $-2.80$  V, this insulating precipitate is reduced to lithium atoms in solid solution with gold, and between  $-2.80$  and  $-3.10$  V a chemically resistant gold + lithium alloy is formed. At potentials more negative than  $-3.10$  V, bulk lithium is formed and reduction of solvent proceeds spontaneously.

Figure 1 shows the SNIFTIRS difference spectrum in a region where one would expect to observe the gold-gold fundamental stretch. Diatomic gold has a vibration frequency of  $190.9 \text{ cm}^{-1}$ , with a reduced mass of  $98.5 \text{ amu}$  [3]. If the gold atom were vibrating with the same force constant against an infinite mass the reduced mass would be  $197 \text{ amu}$ , and a vibrational frequency of  $135 \text{ cm}^{-1}$  would be expected. As the potential is made more negative we observe that the intensity of a band at  $145 \text{ cm}^{-1}$  increases. At these potentials, the surface is being increasingly covered with underpotentially deposited lithium. Due to the sign convention used in these spectra the increase in intensity is an indication of the loss of absorption by a species, here the gold adatom on the gold surface. The close correspondence between the observed  $145 \text{ cm}^{-1}$  frequency and that calculated for a gold atom vibrating against an infinite mass suggests that the adatom is bonded to a single surface atom, that most of the motion involved in the optically active vibration occurs on the adatoms, and that the force constant is nearly the same on the surface as the gas-phase dimer.

At  $440 \text{ cm}^{-1}$  (Fig. 2), a simultaneous and parallel increase in absorbance occurs. This compares to a vibrational frequency of matrix-isolated  $^{197}\text{Au}^{7}\text{Li}$  of  $705 \text{ cm}^{-1}$ . [4]

not 4 missing  
from text.  
Please  
insert.

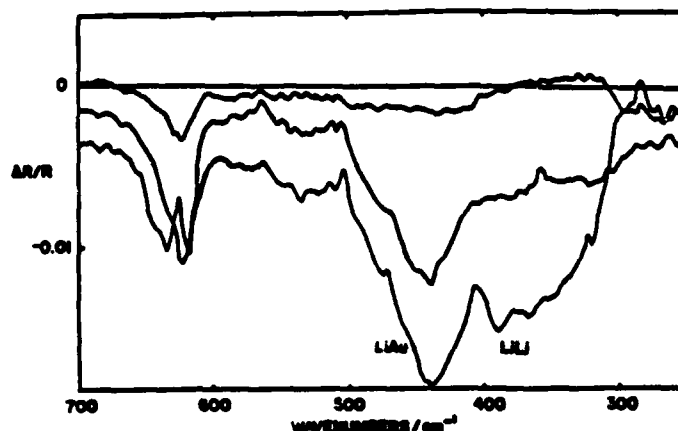


Fig. 2. Surface far infrared difference spectrum of the system described in Fig. 1 in the 200–700  $\text{cm}^{-1}$  region as a function of electrode potential. The curves represent potentials of (top to bottom)  $-1.70$  V,  $-2.90$  V, and  $-3.0$  V respectively. Reference potential  $-1.50$  V.

and probably corresponds to a gold-lithium surface species. The diatomic gold-lithium molecule probably derives much of its high vibrational frequency and large bond strength (2.92 eV) [5] from ionic interactions,  $\text{Li}^+\text{Au}^-$ . This is expected since apart from the halogen atoms, gold has the highest electron affinity of any element (2.31 eV) [6]. On a surface or in the bulk, the electron donated to gold may be delocalized into the gold conduction band, resulting in a smaller Coulombic force between the atoms in Li–Au (surface) than in diatomic Li–Au. Other explanations are possible, of course, but this does explain the lower than expected value for the Li–Au vibrational frequency, however.

No bands attributed to Li–Li vibrations are observed at potentials more positive than those required for bulk deposition of lithium. As soon as three dimensional growth of lithium begins, however, a band at  $395\text{ cm}^{-1}$  rapidly grows in. This may be compared to the  $^7\text{Li}_2$  vibrational frequency of  $351\text{ cm}^{-1}$  in the gas phase [3]. The shift of  $44\text{ cm}^{-1}$  to higher frequency is relatively small considering that it corresponds to condensation of a dimer onto a solid surface. It is therefore probable that the  $395\text{ cm}^{-1}$  peak does correspond to a surface vibration of Li–Li.

A cell was equipped with a very small electrode (0.5 mm diameter) so that the time constant of the cell could be decreased to suitably small values, and time resolved spectra were obtained for the fast nucleation and growth process of lithium on gold. Figure 3a shows the time and wavenumber resolved spectral response obtained at 10 ms intervals following application of the potential. The time profile alone is shown in Fig. 3b. The growth of the absorption transient follows a  $t^3$  dependence (a plot of absorbance/ $t^3$  vs.  $t$  is linear with a correlation coefficient = 0.9989). With this information, one may consider various models of nucleation and crystal growth to determine which possibilities are consistent with this time depend-

ession For

S GRA&I ☒

TAB ☐

ounced ☐

ification

Distribution/

Availability Codes

Avail and/or  
Special

Dist

A-1



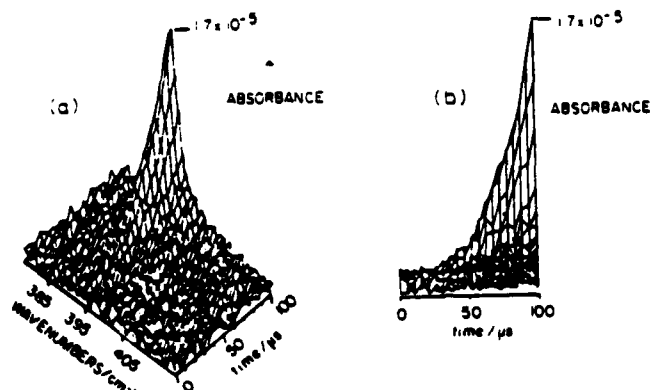


Fig. 3. Time resolved surface far infrared difference spectrum of lithium nucleation and growth. Total experimental time is 100 ms; spectral width is  $45\text{ cm}^{-1}$ , peak is at  $396\text{ cm}^{-1}$ . (a) 3-dimensional plot; (b) time profile of  $395\text{ cm}^{-1}$  peak.

ence. In this particular example, one finds that a mechanism involving instantaneous nucleation of lithium atoms followed by three dimensional growth is consistent with the observed time dependence. One also notes that the absorption peak broadens as it grows, as a result of lateral interactions and surface defects which are incorporated into the new-grown crystallite.

In addition to the metal stretch bands reported in this note, we point out that there are other bands observed in other regions of the infrared spectrum. These correspond to adsorbed supporting electrolyte and solvent, as is evidenced by changing the system components. The behavior and nature of these vibrations will be the subject of a forthcoming report.

In conclusion, we have shown that two new powerful variations of infrared spectroelectrochemistry may be used for the study of a fast reactions at metal surfaces involving direct bonding to the metal surface. Finally, we report the direct observation of metal atom vibrations at surfaces by reflection FTIR spectroscopy.

#### ACKNOWLEDGEMENT

We thank the Office of Naval Research for support of this work.

#### REFERENCES

- 1 J.W. Foley, C. Korzeniewski, J. Daschbach and S. Pons in A.J. Bard (Ed.), *Electroanalytical Chemistry*, Marcel Dekker, New York, in press.
- 2 J. Daschbach, D. Heisler and S. Pons, *Appl. Spectrosc.*, in press.
- 3 K.P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules*, Van Nostrand Reinhold, New York, 1979.
- 4 H.R. Ihle, E. Langenscheidt and B. Zmbora, *J. Chem. Phys.*, 66 (1977) 5105.
- 5 A. Neubert and K.F. Zmbov, *J. Chem. Soc. Faraday Trans.*, 70 (1974) 2219.
- 6 H. Hotop and W.C. Lineberger, *J. Phys. Chem. Ref. Data*, 4 (1975) 539.



DL/413/83/01  
GEN/413-2

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 413 800 N. Quincy Street Arlington, Virginia 22217	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code 5042 Crane, Indiana 47522	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Washington, D.C. 20360	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
DTNSRDC Attn: Dr. G. Bosmajian Applied Chemistry Division Annapolis, Maryland 21401	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 92132	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1		

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. Paul Delahay  
Department of Chemistry  
New York University  
New York, New York 10003

Dr. P. J. Hendra  
Department of Chemistry  
University of Southampton  
Southampton SO9 5NH  
United Kingdom

Dr. J. Driscoll  
Lockheed Palo Alto Research  
Laboratory  
3251 Hanover Street  
Palo Alto, California 94304

Dr. D. N. Bennion  
Department of Chemical Engineering  
Brigham Young University  
Provo, Utah 84602

Dr. R. A. Marcus  
Department of Chemistry  
California Institute of Technology  
Pasadena, California 91125

Dr. J. J. Auburn  
Bell Laboratories  
Murray Hill, New Jersey 07974

Dr. Joseph Singer, Code 302-1  
NASA-Lewis  
21000 Brookpark Road  
Cleveland, Ohio 44135

Dr. P. P. Schmidt  
Department of Chemistry  
Oakland University  
Rochester, Michigan 48063

Dr. Manfred Breiter  
Institut für Technische Elektrochemie  
Technischen Universität Wien  
9 Getreidemarkt, 1160 Wien  
AUSTRIA

Dr. E. Yeager  
Department of Chemistry  
Case Western Reserve University  
Cleveland, Ohio 44106

Dr. C. E. Mueller  
The Electrochemistry Branch  
Naval Surface Weapons Center  
White Oak Laboratory  
Silver Spring, Maryland 20910

Dr. Sam Perone  
Chemistry & Materials  
Science Department  
Lawrence Livermore National Laboratory  
Livermore, California 94550

Dr. Royce W. Murray  
Department of Chemistry  
University of North Carolina  
Chapel Hill, North Carolina 27514

Dr. B. Brummer  
EIC Incorporated  
111 Downey Street  
Norwood, Massachusetts 02062

Dr. Adam Heller  
Bell Laboratories  
Murray Hill, New Jersey 07974

Dr. A. B. Ellis  
Chemistry Department  
University of Wisconsin  
Madison, Wisconsin 53706

Library  
Duracell, Inc.  
Burlington, Massachusetts 01803

Electrochimica Corporation  
20 Kelly Court  
Menlo Park, California 94025-1418

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. M. Wrighton  
Chemistry Department  
Massachusetts Institute  
of Technology  
Cambridge, Massachusetts 02139

Dr. B. Stanley Pons  
Department of Chemistry  
University of Utah  
Salt Lake City, Utah 84112

Donald E. Mains  
Naval Weapons Support Center  
Electrochemical Power Sources Division  
Crane, Indiana 47522

S. Ruby  
DOE (STOR)  
Room 5E036 Forrestal Bldg., CE-14  
Washington, D.C. 20595

Dr. A. J. Bard  
Department of Chemistry  
University of Texas  
Austin, Texas 78712

Dr. Janet Osteryoung  
Department of Chemistry  
State University of New York  
Buffalo, New York 14214

Dr. Donald W. Ernst  
Naval Surface Weapons Center  
Code R-33  
White Oak Laboratory  
Silver Spring, Maryland 20910

Mr. James R. Moden  
Naval Underwater Systems Center  
Code 3632  
Newport, Rhode Island 02840

Dr. Bernard Spielvogel  
U.S. Army Research Office  
P.O. Box 12211  
Research Triangle Park, NC 27709

Dr. Aaron Fletcher  
Naval Weapons Center  
Code 3852  
China Lake, California 93555

Dr. M. M. Nicholson  
Electronics Research Center  
Rockwell International  
3370 Miraloma Avenue  
Anaheim, California

Dr. Michael J. Weaver  
Department of Chemistry  
Purdue University  
West Lafayette, Indiana 47907

Dr. R. David Rauh  
EIC Laboratories, Inc.  
111 Downey Street  
Norwood, Massachusetts 02062

Dr. Aaron Wold  
Department of Chemistry  
Brown University  
Providence, Rhode Island 02192

Dr. Martin Fleischmann  
Department of Chemistry  
University of Southampton  
Southampton SO9 5NH ENGLAND

Dr. R. A. Osteryoung  
Department of Chemistry  
State University of New York  
Buffalo, New York 14214

Dr. John Wilkes  
Air Force Office of Scientific  
Research  
Bolling AFB  
Washington, D.C. 20332

Dr. R. Nowak  
Naval Research Laboratory  
Code 6171  
Washington, D.C. 20375

Dr. D. F. Shriver  
Department of Chemistry  
Northwestern University  
Evanston, Illinois 60201

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. Hector D. Abruna  
Department of Chemistry  
Cornell University  
Ithaca, New York 14853

Dr. A. B. P. Lever  
Chemistry Department  
York University  
Downsview, Ontario M3J1P3

Dr. Stanislaw Szpak  
Naval Ocean Systems Center  
Code 633, Bayside  
San Diego, California 95152

Dr. Gregory Farrington  
Department of Materials Science  
and Engineering  
University of Pennsylvania  
Philadelphia, Pennsylvania 19104

M. L. Robertson  
Manager, Electrochemical  
and Power Sources Division  
Naval Weapons Support Center  
Crane, Indiana 47522

Dr. T. Marks  
Department of Chemistry  
Northwestern University  
Evanston, Illinois 60201

Dr. Micha Tomkiewicz  
Department of Physics  
Brooklyn College  
Brooklyn, New York 11210

Dr. Lesser Blum  
Department of Physics  
University of Puerto Rico  
Rio Piedras, Puerto Rico 00931

Dr. Joseph Gordon, II  
IBM Corporation  
5600 Cottle Road  
San Jose, California 95193

Dr. Nathan Lewis  
Department of Chemistry  
Stanford University  
Stanford, California 94305

Dr. D. H. Whitmore  
Department of Materials Science  
Northwestern University  
Evanston, Illinois 60201

Dr. Alan Bewick  
Department of Chemistry  
The University of Southampton  
Southampton, SO9 5NH ENGLAND

Dr. E. Anderson  
NAVSEA-56Z33 NC #4  
2541 Jefferson Davis Highway  
Arlington, Virginia 20362

Dr. Bruce Dunn  
Department of Engineering &  
Applied Science  
University of California  
Los Angeles, California 90024

Dr. Elton Cairns  
Energy & Environment Division  
Lawrence Berkeley Laboratory  
University of California  
Berkeley, California 94720

Dr. Richard Pollard  
Department of Chemical Engineering  
University of Houston  
Houston, Texas 77004

Dr. M. Philpott  
IBM Corporation  
5600 Cottle Road  
San Jose, California 95193

Dr. Donald Sandstrom  
Boeing Aerospace Co.  
P.O. Box 3999  
Seattle, Washington 98124

Dr. Carl Kannewurf  
Department of Electrical Engineering  
and Computer Science  
Northwestern University  
Evanston, Illinois 60201

Dr. Joel Harris  
Department of Chemistry  
University of Utah  
Salt Lake City, Utah 84112

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. Robert Somoano  
Jet Propulsion Laboratory  
California Institute of Technology  
Pasadena, California 91103

Dr. Johann A. Joebstl  
USA Mobility Equipment R&D Command  
DRDME-EC  
Fort Belvoir, Virginia 22060

Dr. Judith H. Ambrus  
NASA Headquarters  
M.S. RTS-6  
Washington, D.C. 20546

Dr. Albert R. Landgrebe  
U.S. Department of Energy  
M.S. 6B025 Forrestal Building  
Washington, D.C. 20595

Dr. J. J. Brophy  
Department of Physics  
University of Utah  
Salt Lake City, Utah 84112

Dr. Charles Martin  
Department of Chemistry  
Texas A&M University  
College Station, Texas 77843

Dr. H. Tachikawa  
Department of Chemistry  
Jackson State University  
Jackson, Mississippi 39217

Dr. Theodore Beck  
Electrochemical Technology Corp.  
3935 Leary Way N.W.  
Seattle, Washington 98107

Dr. Farrell Lytle  
Boeing Engineering and  
Construction Engineers  
P.O. Box 3707  
Seattle, Washington 98124

Dr. Robert Gotscholl  
U.S. Department of Energy  
MS G-226  
Washington, D.C. 20545

Dr. Edward Fletcher  
Department of Mechanical Engineering  
University of Minnesota  
Minneapolis, Minnesota 55455

Dr. John Fontanella  
Department of Physics  
U.S. Naval Academy  
Annapolis, Maryland 21402

Dr. Martha Greenblatt  
Department of Chemistry  
Rutgers University  
New Brunswick, New Jersey 08903

Dr. John Wasson  
Syntheco, Inc.  
Rte 6 - Industrial Pike Road  
Gastonia, North Carolina 28052

Dr. Walter Roth  
Department of Physics  
State University of New York  
Albany, New York 12222

Dr. Anthony Sammells  
Eltron Research Inc.  
4260 Westbrook Drive, Suite 111  
Aurora, Illinois 60505

Dr. C. A. Angell  
Department of Chemistry  
Purdue University  
West Lafayette, Indiana 47907

Dr. Thomas Davis  
Polymer Science and Standards  
Division  
National Bureau of Standards  
Washington, D.C. 20234

Ms. Wendy Parkhurst  
Naval Surface Weapons Center R-33  
R-33  
Silver Spring, Maryland 20910

DL/413/83/01  
359/413-2

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. John Owen  
Department of Chemistry and  
Applied Chemistry  
University of Salford  
Salford M5 4WT ENGLAND

Dr. Boone Owens  
Department of Chemical Engineering  
and Materials Science  
University of Minnesota  
Minneapolis, Minnesota 55455

Dr. J. O. Thomas  
University of Uppsala  
Institute of Chemistry  
Box 531  
S-751 21 Uppsala, Sweden

Dr. O. Stafsudd  
Department of Electrical Engineering  
University of California  
Los Angeles, California 90024

Dr. S. G. Greenbaum  
Department of Physics  
Hunter College of CUNY  
New York, New York 10021

Dr. Menahem Anderman  
W.R. Grace & Co.  
Columbia, Maryland 20144

END

DATE

FILMED

6-1988

DTIC